Nitrosoalkenes: Synthesis and Properties of Nitroso Derivatives of a Vinylogous Tetrathiafulvalene

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Introduction

The chemistry of nitrosoalkenes is much less developed than that of nitrosoarenes and nitrosoalkanes.¹ Nitrosoalkenes are generally unstable,² and their generation has usually been established by trapping with an appropriate Diels–Alder diene. A few stable, crystalline monomeric nitrosoalkenes have been reported, however,^{3–8} almost all of which are nitrosodithiafulvenes or -diselenafulvenes, systems in which the nitroso group is stabilized by electron donation of the chalcogen atoms.

We now report the synthesis of the first nitroso derivatives (3, 16, and 17) of a vinylogous tetrathiafulvalene (18) and some novel properties of these compounds.

Results and Discussion

The intensely purple compound **3** was obtained in good yield by the Wittig reaction of the ylide of phosphonium salt 2^9 with the readily prepared 2-(nitrosoformylmethylene)-4,5-dicarbomethoxy-1,3-dithiole (**1**)⁷ in the presence of triethylamine at rt. No product derived from ylide attack at the nitroso group of **1** was detected.

Careful treatment of **3** with 1 mol equiv of tributylphosphine at rt led to an immediate reaction with the formation of the novel red imine **4** in 57% yield. The reaction also yielded the vinylic nitrile **5**, a product of the reductive cleavage of the starting nitroso compound **3**. This result parallels our work with 2-(nitrosophenylmethylene)-4,5-dicarbomethoxy-1,3-dithiole (**7**) which was reported earlier.¹⁰ Deoxygenation of **7** was postulated to lead to a nitrene, which fragmented to produce benzonitrile and tetrakis(carbomethoxy)tetrathiafulvalene (**9**), *via* carbene **8**.

By analogy, the formation and fragmentation of nitrene **10** should lead to the nitrile **5** and the carbene **8**. In

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contrast to the earlier case of **7** (Scheme 1), carbene **8** couples preferentially with nitrene **10**, rather than dimerizing to tetraester **9**. Interestingly enough, no trace of the azo derivative **11**, a plausible dimerization product of nitrene **10**, was detected, and only traces of the tetraester **9** were found (Scheme 2).

It would appear that nitrene **10** may have a longer lifetime than usual, allowing it to act as an efficient trap for carbene **8**. Stabilization of **10** could be achieved by sulfur participation, as in the resonance contributor **10a**. The intermediacy of the carbene **8** was established by

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Scheme 3

running the experiment in the presence of benzaldehyde. This reaction produced imine **4**, and nitrile **5** as well as the known compound **6**⁹ in reasonable yield (Scheme 1). Our proposal for the mechanism of this reaction is further strengthened by the fact that the reaction is concentration dependent. Dilution decreases the yield of imine quite significantly. When the less reactive oxygen abstractor triphenylphosphine was used in the reaction, imine **4** was obtained, but at a much slower rate.

Attempts at the formation of imine **4** by an aza-Wittig reaction of the nitroso compound **3** with the phosphonium salt **2** and triethylamine were unsuccessful. We also conceived that a second mole of tributylphosphine could form the reagent **12** which, on reaction with benzalde-hyde, would produce imine **13**. The reaction with 2 mol of tributylphosphine, however, produced compounds **5** and **6**, none of compound **13**, and a very small amount of imine **4**. We also observed that use of any excess phosphine resulted in a decrease of imine **4** (Scheme 3).

Reaction of the nitrosoester **3** with *m*-chloroperbenzoic acid (*m*-CPBA) produced none of the analogous nitroester **15**. This was, however, available in excellent yield as shown in Scheme 4.

Thus, oxidation of compound **1** took place preferentially at the nitroso function, and the emerald green nitroso aldehyde was converted smoothly by *m*-CPBA into yellow-green crystals of the nitro aldehyde **14** in 76% yield. Nitro aldehyde **14** underwent a Wittig reaction with the ylide of phosphonium salt **2** to produce the desired **15** as red crystals.

The reaction of **3** with isoamyl nitrite afforded a brown compound, mp 182 °C, the analysis and mass spectrum of which were consistent with the dinitroso structure **16**. However, true vicinal dinitroso compounds appear to be unknown, and attempts to obtain such compounds generally lead to very stable 1,2,5-oxadiazole *N*-oxides.¹¹



There is literature precedence for 1,2,5-oxadiazole N-oxides (*viz.* **16b**)¹¹ and stabilization of nitroso compounds of this type by nonbonded S- - O interactions is well known.^{7,8} The proton NMR spectrum of **16** leads us to believe that the bis-nitroso compound exists in the form **16a** since there are only two singlets in its proton NMR spectrum in a ratio of 1:1, implying a symmetrical molecule. We have so far not succeeded in obtaining suitable crystals of this compound so as to verify the structure by X-ray crystallographic measurements.

Formation of **16** by this method is always accompanied by production of the nitroso nitro analog **17**. Hence, treatment of **3** with 2 mol equiv of isoamyl nitrite produced, after 3.5 h at rt, green crystals of compound **17** in 46% yield, and the bis-nitroso compound as a brown powder in 25% yield. When the reaction was carried out using **8** mol equiv of isoamyl nitrite, only a trace of **16** was formed, and the nitroso nitro compound was the dominant product (Scheme 5).

The same compound **17** is also obtained in 83% yield by treatment of the nitro ester **15** with excess isoamyl nitrite, and by the reaction of ethanediylidene-2,2'-bis-(4,5-dicarbomethoxy-1,3-dithiole) (**18**) with nitrous acid or with isoamyl nitrite (Scheme 6). Formation of **17** from **18** could be shown to always proceed via the nitro compound **15**, rather than *via* the nitroso analog **3**.

We note with interest the difference in reactivity between the nitroso function of the aldehyde **1** and that of the compound **3** and continue our investigations in this area.

Experimental Section

General. All melting points are uncorrected. UV-visible spectra were determined in CH_2Cl_2 . The NMR spectra were determined in $CDCl_3$ at 360 MHz. Elemental analyses were carried out by Atlantic Microlabs, Atlanta, GA.

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2-(Nitroformylmethylene)-4,5-dicarbomethoxy-1,3-dithiole (14). To a solution of the nitrosoaldehyde⁷ (1, 0.50 g, 1.73 mmol) in CHCl₃ (15 mL) was added sodium bicarbonate (0.60 g). A solution of m-CPBA (48%, 0.865 g, 2.4 mmol) in CHCl₃ (20 mL) was then added dropwise over 30 min to the above mixture, with stirring at rt. The mixture was stirred at rt for a further h after which it was diluted with CHCl₃ (50 mL) and water (20 mL). The chloroform solution was washed successively with thiosulfate solution and water and was dried and concentrated. Trituration of the resultant yellow-green solid with cold methanol produced crystalline 14 (0.40 g, 76%): mp 136-137 °C (CH₂Cl₂/MeOH); UV-vis λ_{max} 207 nm (log ϵ 3.36), 217 (3.41), 240 (3.40), 309 (3.32), 388 (3.95); ¹H NMR 4.01 and 4.00 (each 3H, s), 10.35 (1H, s, CHO); mass spectrum, m/z (relative intensity) 305 (12, M⁺), 258 (39), 244 (100). Anal. Calcd for C₉H₇NO₇S₂: C, 35.41; H, 2.31; N, 4.59; S, 21.01. Found: C, 35.47; H, 2.28; N, 4.56; S, 20.94.

2,2'-(2-Nitrosoethanediylidene)bis(4,5-dicarbomethoxy-1,3-dithiole) (3). To a solution of nitrosoaldehyde (1, 3.00 g, 10.38 mmol) in CH₂Cl₂ (60 mL) was added triethylamine (4.0 mL). To this solution was added 4,5-dicarbomethoxy-1,3-dithiol-2-yltributylphosphonium tetrafluoroborate⁹ (2, 6.06 g, 11.93 mmol) in small portions with stirring, while the mixture was cooled in an ice bath. Addition was completed in 20 min, the cooling bath was removed, and the mixture was stirred for a further 1 h. The solvent was evaporated, methanol was added, and the dark purple crystals were collected (3.84 g, 75%): mp 177–179 °C (CH₂Cl₂/MeOH); UV-vis λ_{max} 220 nm (log ϵ 4.29), 229 (4.32), 254 (4.23), 277 (4.09), 367 (4.44), 568 (3.76); ¹H NMR 3.98 (6H, s), 3.87 (3H, s), 3.83 (3H, s), 6.76 (1H, s, H); mass spectrum, *m*/*z* (relative intensity) 491 (0.2, M⁺), 257 (100), 206 (31). Anal. Calcd for $C_{16}H_{13}NO_9S_4$: C, 39.10; H, 2.66; N, 2.85; S, 26.09. Found: C, 39.02; H, 2.69; N, 2.78; S, 25.97.

Compounds 4 and 5. Tributylphosphine (0.2 mL, 8×10^{-4} mol) was added dropwise, via syringe, to a stirred solution of the nitroso ester (**3**, 0.40 g, 8×10^{-4} mol) in CH₂Cl₂ (10 mL). The purple solution became bright orange-red in color. The mixture was stirred at rt for 5 min; the solvent was evaporated at rt, methanol was added, and the resultant dark red powder (**4**) was collected (0.160 g, 57%); mp 223 °C (dec); after crystallization from CHCl₃/MeOH mp 235–6 °C; UV-vis λ_{max} 219 nm (log ϵ 4.53), 230 (4.55), 301 (4.27), 371 (4.21), 386 (sh, 4.18), 471 (4.43); ¹H NMR 3.92 (6H, s), 3.88 (9H, s), 3.85 (3H, s), 7.35 (1H, s, H); mass spectrum, m/z (relative intensity) 693 (9, M⁺), 436 (20), 378 (61), 357 (51). Anal. Calcd for C₂₃H₁₉NO₁₂S₆: C, 39.82; H, 2.62; N, 2.02; S, 27.73. Found: C, 39.60; H, 2.80; H, 2.03; S, 27.97.

Removal of the solvent from the methanol-soluble portion, followed by chromatography (SiO₂, CHCl₃) yielded 2-(cyanomethylene)-4,5-dicarbomethoxy-1,3-dithiole as yellow crystals (**5**, 0.098 g, 48%). Recrystallization from CHCl₃-hexane yielded shiny yellow crystals of **5**: mp 108–110 °C; UV-vis λ_{max} 205 nm (log ϵ 3.60), 222 (sh, 3.74), 230 (3.77), 310 (4.17), 327 (sh, 4.01) 359 (3.32); ¹H NMR 3.88 (3H, s), 3.87 (3H, s), 5.24 (1H, s); mass spectrum, m/z (relative intensity) 257 (100, M⁺). Anal. Calcd for C₉H₇NO₄S₂: C, 42.01; H, 2.74; N, 5.44; S, 24.92. Found: C, 41.90; H, 2.67; N, 5.40; S, 24.88. When the same deoxygenation of **3** was carried out in the presence of 1 equiv of benzaldehyde, compounds **4**, **5**, and **6**⁹ were obtained in yields of 30%, 57%, and 23%, respectively.

2,2'-(2-Nitroethanediylidene)bis(4,5-dicarbomethoxy-1,3-dithiole) (15). To a solution of nitro aldehyde (14, 0.38 g, 1.25 mmol) in CH₂Cl₂ (8 mL) was added triethylamine (0.5 mL). To this solution was added the phosphonium salt (2, 735 mg, 1.45 mmol) in small portions, in the course of 15 min with stirring, while the mixture was cooled in an ice bath. On addition of the salt there was an immediate color change from yellow-green to orange-red. The cooling bath was removed, and the mixture was stirred for a further 20 min. Removal of the solvent followed by addition of methanol yielded 15 as a red powder (0.54 g, 86%): mp 132-134 °C (CH₂Cl₂/MeOH); UV-vis $\hat{\lambda}_{\max}$ 221 nm (log ϵ 4.98), 229 (4.99), 302 (4.84), 384 (4.90), 440 (sh, 4.64); ¹H NMR 3.96, 3.95, 3.88, 3.84 (each, 3H, s), 6.17 (1H, s, H); mass spectrum, m/z (relative intensity) 507 (15, M⁺), 461 (48), 243 (100). Anal. Calcd for C₁₆H₁₃NO₁₀S₄: C, 37.86; H, 2.58; N, 2.76; S, 25.27. Found: C, 37.80; H, 2.57; N, 2.72; S, 25.15

2,2'-(2,2'-Dinitrosoethanediylidene)bis(4,5-dicarbomethoxy-1,3-dithiole) (16). To a solution of compound **3** (500 mg, 1.02 mmol) in CH_2Cl_2 (35 mL) was added isoamyl nitrite (0.27 mL, 2.04 mmol), and the mixture was stirred at rt under an atmosphere of nitrogen for 3.5 h. The solvent was removed, the residue was treated with boiling methanol, and the resultant dark brown precipitate was collected by filtration.

The methanol-soluble portion was concd and purified by chromatography (SiO₂, CHCl₃:EtOAc 10:1) to give **17** (245 mg, 46%). The brown powder was treated successively with hot benzene–CH₂Cl₂ (1:1) and hot acetone in an effort to remove starting material, the sole contaminant. Soxhlet extraction with CHCl₃ then left behind pure **16** (135 mg, 25%): mp 182 °C; UV-vis λ_{max} 224 nm (log ϵ 4.46), 244 (4.50), 329 (4.13), 468 (4.23); ¹H NMR 4.04 and 4.01 (each 6H, s); mass spectrum, m/z (relative intensity) 520 (0.2, M⁺), 460 (1.5), 250 (34), 206 (88), 178 (100). Anal. Calcd for C₁₆H₁₂N₂O₁₀S₄: C, 36.92; H, 2.32; N, 5.38. Found: C, 36.75; H, 2.32; N, 5.25.

2,2'-(2-Nitro-2'-nitrosoethanediylidene)bis(4,5-dicarbo-methoxy-1,3-dithiole) (17). (a) From **15**: Isoamyl nitrite (0.2 mL, 1.49 mmol) was added to a solution of the nitro ester (**15**, 40 mg, 7.9×10^{-5} mol) in CH₂Cl₂ (4 mL), and the mixture was stirred at rt under nitrogen. On addition of isoamyl nitrite the color of the solution changed from red through yellowish-brown to yellowish green. After 15 min, the solvent was removed, methanol was added, and the mixture was cooled with stirring. Compound **17** was obtained as a green precipitate (35 mg, 83%): mp 177 °C (benzene/hexane); UV-vis λ_{max} 219 (log ϵ 3.56), 238 (3.55), 381 (sh, 3.44), 415 (3.64); ¹H NMR 4.02, 3.99, 3.97, 3.86 (each, 3H, s); mass spectrum, m/z (relative intensity) 536 (1.5, M⁺), 250 (52), 234 (55), 206 (100). Anal. Calcd for C₁₆H₁₂N₂O₁₁S₄: C, 35.82; H, 2.24. Found: C, 35.76; H, 2.32.

(b) From **18**: To a cold solution of 2,2'-ethanediylidenebis-(4,5-dicarbomethoxy-1,3-dithiole) (**18**, 0.92 g, 1.99 mmol) in CH₂-Cl₂ (25 mL) was added a solution of sodium nitrite (300 mg, 4.35 mmol) in H₂O (10 mL). Excess 3 M HCl was added to the mixture while being cooled in an ice-bath. The color of the reaction mixture changed to light red, and TLC showed the absence of starting material. Urea was added to quench any traces of HNO₂, the organic layer was concentrated, and the residue was triturated with methanol. The brown crystals obtained were purified by chromatography (SiO₂, benzene:CHCl₃ 3:1) to produce green crystals of **17** (310 mg, 29%). Concentration of the methanol-soluble portion followed by chromatography (SiO₂, CH₂Cl₂) yielded (**15**) (400 mg, 40%).

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